

FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

Thomas J. Houser, Michael E. McCarville and Gu Zhuo-Ying

Chemistry Department, Western Michigan University
Kalamazoo, MI 49008

INTRODUCTION

Combustion of fossil fuels in large stationary furnaces causes the emission of nitrogen oxides, a large fraction of which arise from the nitrogen-containing components in the fuel, producing a major pollution problem which is expected to increase in severity in the future. The results being reported in this paper are part of those obtained from a continuing study to determine the mechanism by which these oxides may form. Because studies have shown that most of the nitrogen in heavy oils is in the form of heterocycles (1-3) and it is believed that the nitrogen components of coal are similar, pyridine was selected as representative of these components. It was assumed that the radical fragments formed during pyridine pyrolysis and rich, low temperature oxidation would be similar to those obtained from the same reactions of fossil fuels that occur during the pre-flame stages of combustion. Later experiments emphasized HCN oxidation since several studies indicated that it was the key volatile, nitrogen-containing intermediate formed during fuel nitrogen combustion (4-8). In addition, HCN used with several fuel additives allowed a greater control of the chemical nature of the reaction environment. We have previously reported on the inert pyrolysis kinetics of pyridine (9), the rate of formation of HCN during pyridine pyrolysis (10), the oxidation kinetics of cyanogen (11), and of pyridine (12) and HCN (13) at low temperatures.

EXPERIMENTAL

A flow system designed to operate at atmospheric pressure was constructed for the study of the oxidation of the pertinent nitrogen-containing reactants. The system is suitable for the introduction of volatile liquids (reactants and solutions with additives) into a heated helium stream through the use of a syringe pump to drive a calibrated, tuberculin syringe. The system can also utilize gaseous species; these reactants and additives, mixed with helium at the desired concentrations, are maintained in steel storage tanks. The flow stream is examined by a quadrupole mass analyzer equipped with capillary probe atmospheric sampler which functioned as an on stream monitor for the consumption of reactants. Helium is used as the carrier gas because it is chemically inert and has a very high thermal conductivity, thus providing rapid heating and quenching. The system has a group of removable Vycor reactors heated by an electric furnace. One reactor was a stirred-flow design (40 cc) which had been previously tested for stirring efficiency (14), the others were plug-flow type (10 to 40 cc). A flow line which bypasses the reactor was used so that entrance and exit concentrations of reactants could be measured. A Thermo Electron Chemiluminescent NO/NO_x analyzer with on stream sampling was used for the oxidation studies of pyridine, HCN and N₂O. A modification of the flow stream was required to obtain direct samples from the reactor effluent to measure the light gases with a gas chromatograph. A linear switching valve was used to provide a series-bypass capability with

constant back pressure for the two columns. A molecular sieve 5A column was used for O_2 , N_2 and CO while a porous polymer Chromosorb 101 column was used for CO_2 and N_2O . In order to determine the amounts of HCN and NH_3 produced from the oxidation of pyridine and HCN, dilute solutions of NaOH or HCl in the bubble towers were used in separate experiments to trap the HCN or NH_3 respectively, for ion-specific electrode analysis. A second bubbler in series with the first was found to be unnecessary.

RESULTS AND DISCUSSION

The current study has shown that in order to produce significant yields of NO from the oxidation of pyridine or HCN-fuel mixtures, conditions which promote a flame must exist in the flow reactor. The existence of a flame was confirmed by visual observation in several, but not all, experiments. The capability of producing a flame depends on the nature of the fuel (Tables 1, 2 and 3, all data are stirred-flow), temperature (Tables 1, 2, 3 and 5), concentrations (Tables 1-5), reactor design (stirred - or plug-flow, Table 5), and flow rate (Tables 1 and 5). The conditions which promoted NO formation were characterized by complete consumption of fuel-nitrogen at all flow rates in the stirred-flow reactor, however, the plug-flow reactor exhibited an inverse consumption at intermediate temperatures, at first decreasing from complete consumption at high flows, passing through a minimum then increasing again (Table 5, C_5H_5N and HCN/C_6H_6 mixtures at 800 C and HCN/CO at 700 C) while the NO yield continually decreased. After a threshold temperature was reached in the plug-flow reactor, the NO yield did not appear to depend on temperature significantly (Table 5). The non-flame conditions, at relatively low temperatures and/or concentrations of fuels, were characterized by a flow rate dependent consumption of fuel-nitrogen which was converted essentially completely to N_2 and N_2O (maximum yield of about 50% of the latter) (12, 13). This was observed in both types of reactors, however, the flame condition persisted to a much lower temperature in the entrance of the plug-flow reactor as evidenced by visual observation and NO production. The observed dependence of NO yields on flow rate, first increasing to a maximum then decreasing (Tables 1, 2 and 5) in the stirred-flow reactor was not observed with plug-flow, thus is thought to be an anomaly due to reactor-induced flame instability. However, other yield dependencies are qualitatively the same in both types of reactors. The transition between flame and non-flame reaction was abrupt as evidenced by a rapid increase in fuel nitrogen consumption and shift in products, thus is attributed to a change in mechanism rather than a sequential process.

Specifically it was found that pyridine and benzene/HCN mixtures give similar results (Tables 1, 2 and 5) while CO (Tables 2 and 5) and acetylene (13) added to HCN promoted NO formation at lower temperatures and concentrations (on an atom or heat equivalent basis), than the other fuel combinations. Mixtures of H_2/HCN were very different from other fuel combinations, producing lower extents of HCN consumption and very low to negligible yields of NO at conditions which normally gave high yields of NO with other fuels (Table 1). Finally, it has been clearly established that N_2O was the prevalent oxide of nitrogen at low temperatures (Table 5 and Reference 15) and/or equivalence ratios (Table 4), whereas NO became prevalent at higher temperatures and fuel concentrations (up to stoichiometric mixtures) and that their concentrations were inversely related. In order to further check the possibility of NO/ N_2O interconversion experiments were performed by adding NO_2 (NO did not exist in our reactant storage tank) to the

reaction mixture at low temperatures and by oxidizing N_2O in the presence of various fuels (Table 7). The results with NO were somewhat inconclusive since some experiments showed some increase in N_2O and others did not (16). The relatively small increases observed indicate that NO/NO_2 could not be a major source of N_2O at those conditions. The results with N_2O clearly show that NO is not formed from N_2O in large yields.

In addition to the volatile products observed, it was noted that a white solid was formed (about a 3% yield) at non-flame conditions with lean mixtures of $HCN/CO/O_2$ and $HCN/H_2/O_2$. Samples of these solids were examined by infrared and elemental analyses which indicated that those from HCN/CO were NH_4NCO , whereas most, but not all, of those from HCN/H_2 were urea (Table 8). It was also found that a room temperature sublimate from NH_4NCO was urea, indicating an easy conversion was possible. These solids show the presence of NH_3 and $HNCO$ in the reactor at non-flame conditions. In an attempt to determine the nature of the intermediate that leads to N_2O formation, oxidation studies of methylisocyanate and dimethylhydrazine, with and without additive fuels, were made. No increase in N_2O formation was noted from these over that obtained from HCN.

CONCLUSIONS

The conclusions reached from the above observations are: (1) That N_2O and NO are probably formed from a common precursor in the mechanistic chain, although possibly not the same immediate intermediate, and neither are formed from each other. The data strongly shows that NO does not form at those lower temperatures which promote N_2O formation and N_2O does not oxidize to NO. In addition, the equivalence ratio dependence shows that N_2O forms at leaner conditions than does NO, which is most likely due to maintenance of flame conditions at the more rich conditions. Thus, the reported mechanism steps for the formation of N_2O from NO, at least at our conditions, are not applicable (17). (2) That NO formation cannot occur primarily by an interaction between NH or N and OH, as usually assumed in mechanisms (17), because of the observed influence of different fuels on the conditions necessary to produce NO.

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TABLE 1 Fuel Type Effects on NO Yields (% of Reacted N) at 950 C
Reactants - Initial Concentrations (mole %)

Time(sec)	ERA	<u>.9C₅H₅N/70₂</u>	<u>1HCN/.5C₆H₆/70₂</u>	<u>1HCN/3CO/70₂</u>	<u>1HCN/3H₂/70₂</u>	<u>1HCN/3H₂/60₂^b</u>
		.87	.79	.46	.46	.54
0.375		13	18	42	--	0.4
0.5		12	26	35	0.5	0.3
0.75		27	67	34	--	--
1.0		69	66	32	0.3	0.2
2.0		44	42	19	--	--
4.0		6	14	5	--	--

Time(sec)	ERA	<u>.5C₅H₅N/70₂</u>	<u>.2HCN/.25C₆H₆/3.50₂</u>	<u>2HCN/5CO/70₂</u>	<u>2HCN/140₂</u>	<u>2HCN/70₂</u>
		.48	.64	.86	.25	.50
0.375		17	--	--	--	--
0.5		24	24	70	2.0	2.1
1.0		32	26	60	2.2	5.0
2.0		44	52	35	1.1	5.5
4.0		24	29	14	0.5	2.8

(a) Equivalence ratios were calculated on the basis of CO₂, H₂O and NO as products

(b) These were run at 900 C

TABLE 2 Temperature Effects on NO_x Yield (% of Reacted N) for Various Fuels

Time(sec)	<u>.9C₅H₅N/70₂(.87)^a</u>		<u>.5C₅H₅N/70₂(.48)</u>		<u>1HCN/.25C₆H₆/70₂(.52)</u>	
	900 C	950 C	900 C	950 C	900 C	
0.5	6	12	13	24	5	
0.75	14	27	--	--	--	
1.0	20	69	13	32	6	
1.5	10	54	--	56	--	
2.0	7	44	9	44	5	
4.0	--	6	12	24	3	

	<u>.25HCN/.2C₆H₆/3.50₂(.53)</u>			<u>2HCN/4CO/70₂(.79)</u>		
	925 C	950 C	1000 C	800 C	900 C	1000 C
0.5	15	24	--	8	40	56
1.0	15	26	96	8	41	52
2.0	12	52	80	2	30	48
4.0	--	29	44	--	--	26

	<u>1HCN/6CO/120₂(.40)</u>			<u>1HCN/8CO/120₂(.48)</u>	
	700 C	800 C	900 C	700 C	800 C
0.5	2	29	70	7	46
1.0	4	62	66	27	80
2.0	2	56	56	70	69
4.0	--	20	20	1	27

(a) Reactant concentrations and (equivalence ratios) are the same basis as in Table 1

TABLE 3 Fuel Rich NO_x Yields (% Reacted N)

Time(sec)	<u>.65C₅H₅N/3.5O₂(1.25)^a</u>	<u>1HCN/8CO/3O₂(1.92)</u>	
	1000 C ^b	800 C	900 C
0.5	12	6	55
1.0	22	7	51
2.0	22	1	30
4.0	12	0.2	8
	<u>1HCN/4CO/2O₂(1.88)</u>	<u>1HCN/5CO/4O₂(1.06)</u>	
	1000 C	800 C	900 C
0.5	3	10	48
1.0	4	33	44
2.0	2	24	32
4.0	--	3	10

(a) See Table 1 footnote (a) for ER calculation

(b) Yields were negligible for this mixture at 900 C

TABLE 4 Equivalence Ratio Effects on NO_x/N₂O Yields

% C ₆ H ₆ ^a	ER	Yield NO _x /N ₂ O ^b	
		Stirred (775 C)	Plug (800 C)
0	0.25	0.7/29	0.2/30
0.12	0.38	0.5/39	--
0.25	0.52	0.4/40	0.2/28
0.5	0.79	0.5/34	12/14
0.75	1.05	1.1/23	26/2
1.00	1.32	2.5/1.2	24/--

(a) Reactants are 1HCN/7O₂ plus benzene in mole % - ER as in Table 1, footnote (a)

(b) Both stirred and plug flow reactors were used with one second contact time for all experiments

TABLE 5 Comparison of Plug and Stirred-Flow Data:
NO/N₂O Yields in % Reacted Nitrogen

Time(sec)	<u>1HCN/.25C₆H₆/70₂^a</u>					
	<u>800 C</u>		<u>900 C</u>		<u>950 C</u>	
	Plug	Stirred	Plug	Stirred	Plug	Stirred
0.25	40/13	--	39/22	--	39/10	10/--
0.5	16/25	n/45	16/22	5/41	29/13	15/--
1.0	n/30	n/40	3/45	6/39	10/15	46/--
2.0	n/34	n/43	n/8	5/33	1/11	28/--
4.0	n/28	n/40	n/8	3/31	n/5	11/--

	<u>.5C₅H₅N/70₂</u>					
	<u>725 C</u>	<u>800 C</u>		<u>900 C</u>		<u>950 C</u>
	Plug	Plug	Stirred	Plug	Stirred	Plug Stirred
0.25	--	56/6	--	--	--	56/6 --
0.5	n/n	34/18	n/--	42/12	13/28	40/8 24/--
1.0	4/3	9/33	--	18/24	13/30	19/13 32/--
2.0	3/32	n/37	--	4/26	9/30	5/10 44/--
4.0	5/43	n/40	--	--	12/26	1/5 24/--

	<u>1HCN/4CO/60₂^b</u>					
	<u>700 C</u>		<u>750 C</u>		<u>800 C</u>	
	Plug	Stirred	Plug	Stirred	Plug	Stirred
0.25	40/5	--	--	--	35/1	--
0.5	17/11	n/--	21/7	1/37	32/3	9/13
1.0	3/26	n/28	21/11	2/37	16/22	33/18
2.0	n/32	n/27	n/14	1/40	n/36	23/22
4.0	n/22	n/25	n/--	--	n/23	2/22

- (a) Compositions in mole %, n is for negligible amounts
 (b) For CO added fuels below 700 C the HCN consumption dropped drastically and was time dependent, whereas, above 700 C the HCN was more than 90% consumed at all flow rates

TABLE 6 Low Temperature - Pyridine Oxidation (Plug Flow Reactor)
% Yields of HCN/N₂O

<u>.5C₅H₅N/70₂^a</u>			
Time(sec)	<u>750 C</u>	<u>725 C</u>	
0.25	68/n	--	--
0.5	11/48	30/n	--
1.0	2/55	58/3	47/n
2.0	--	16/32	9/50
4.0	--	2/43	7/48
<u>800 C</u>			
NO _x high at .25 and .5 sec. HCN negligible at all flows			
(a) Concentrations in mole %			

TABLE 7 N₂O Oxidation Data
% N₂O Reacted/NO_x Yield (% of Reacted N₂O)^a

		<u>2.2N₂O/70₂^b</u>		<u>2.2N₂O/8C0/70₂</u>		<u>2.2N₂O/.5C₆H₆/70₂</u>
Time(sec)		900 C	1000 C	900 C	1000 C	1000 C
0.5	10/13	53/12	84/14	94/18	--	--
1.0	20/9	80/9	79/11	91/14	91/9	--
2.0	33/9	91/7	76/9	98/8	--	--
4.0	54/3	92/5	83/5	99/6	99/3	--
(a) Similar low yields of NO _x were found at 800 and 750						
(b) Concentrations in mole %						

TABLE 8 Solids Formation

<u>%N-Fuel Reacted</u>	<u>Temperature (C)</u>	<u>Principal Solid Product</u>
<u>2HCN/8C0/70₂</u>		
15	650	NH ₄ NCO
18	650	NH ₄ NCO
17	650	NH ₄ NCO
40	675	NH ₄ NCO
<u>2HCN/4H₂/70₂</u>		
50	650	Urea
29	700	Urea
20	600	NH ₄ NCO
<u>2C₅H₅N/70₂</u>		
97	750	NH ₄ NCO